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# THE DEVELOPMENT OF STRUCTURAL ADHESIVE SYSTEMS SUITABLE FOR USE WITH LIQUID OXYGEN

by

Floyd D. Trischler and Alfred McLeod

## SUMMARY REPORT VI

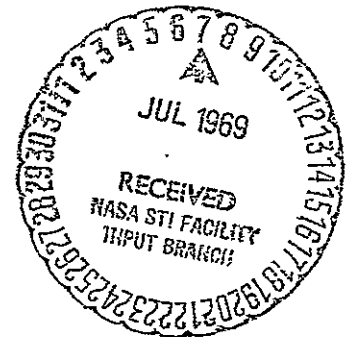
Covering Period 1 May 1968 to 5 December 1968

27 December 1968

Prepared under Contract No. NAS 8-11068  
Control No. DCN-1-8-54-10172(1F)

by

WHITTAKER CORPORATION  
Research & Development/San Diego  
San Diego, California 92123



FACILITY FORM 602	N69-40782	
	(ACCESSION NUMBER)	(THRU)
	56	1
	(PAGES)	(CODE)
	CA-102259	27
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Propulsion and Vehicle Engineering Division  
National Aeronautics and Space Administration  
George C. Marshall Space Flight Center  
Huntsville, Alabama

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Floyd D. Trischler and Alfred, McLeod

SUMMARY REPORT VI

Covering Period 1 May 1968 to 5 December 1968

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Prepared under Contract No. NAS 8-1106

Control No. DCN-1-8-54-10172(1F)

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National Aeronautics and Space Administration  
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FOREWORD

This report was prepared by Whittaker Corporation, Research & Development/San Diego, under Contract No. NAS 8-11068, Control No. DCN-1-8-54-10172(1F), entitled "The Development of Structural Adhesive Systems Suitable for Use With Liquid Oxygen," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Astronautics Laboratory, Materials Division, with Dr. W. E. Hill acting as project officer.

The research work was conducted in our laboratory by Messrs. Floyd D. Trischler, Senior Chemist; Edward S. Harrison and Alfred McLeod, chemists; and James Charter, H. Wooster and William Warner, senior technicians. Mr. Trischler served as program manager. This report covers the period from 1 May 1968 to 5 December 1968.

Prepared by: Floyd D. Trischler  
Floyd D. Trischler

Approved by: Rex B. Gosnell  
Rex B. Gosnell

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#### ABSTRACT

Quality control tests were developed and utilized to obtain more valid test results from the monomers and prepolymers used on this program. In order to obtain consistent adhesive test results, a standardized bonding procedure was developed. A computer program was devised to evaluate the effect of compositional variables on bond strength. In addition, the effect of surface preparation and the use of primers on adhesive performance was investigated.

Processing and scale-up studies were completed on the materials used for this program, with a resultant improvement in yields and batch size of products.

The conditions necessary to prepare a storage-stable isocyanate-terminated prepolymer of perfluoropropylene oxide were defined. In addition, a brief study was conducted on amine curing agents for this prepolymer.

Various parameters involved in the optimization of the fluorinated polyurethane as an adhesive were investigated. These included the effect of catalyst, catalyst concentration, temperature, filler, and crosslink density. This adhesive was found to be LOX compatible.

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## INTRODUCTION AND SUMMARY

The present and planned use of liquid oxygen (LOX) in space vehicles has created an urgent requirement for materials that are compatible with LOX. The development of LOX-compatible adhesives having structural utility at cryogenic temperatures is especially desired for application in critical bonding operations.

Before this contract, polymers resistant to LOX and usable as adhesives were not available. The intent of this program was to develop polymers especially suited for but not limited to adhesive formulation. Since polyurethanes are noted for their outstanding cryogenic properties, emphasis was placed on the preparation of highly halogenated polyurethanes and the requisite monomers.

Fundamental research was carried out to obtain the following information on the LOX compatibility of polymers: (1) the type and amount of halogen necessary to impart LOX compatibility to candidate polymers, and (2) the effect of different functional groups and other structural features on the LOX compatibility of various polymers with similar halogen content. The polymers prepared previously on this program were designed to provide the most basic information of this nature.

The polyurethane from hexafluoropentanediol and various perhalogenated diisocyanates were found to be stable to impact in LOX. Considerable work was conducted to lengthen the diol portion of the polyurethane in order to impart useful low temperature properties. A number of polymeric polyols were prepared and evaluated. Of these, the polyether of perfluoropropylene oxide diol was outstanding. Polyurethanes prepared from this diol were promising as adhesives and showed resistance to LOX.

Various diisocyanates were investigated in the preparation of polyurethanes from the polyether of perfluoropropylene oxide. 1-Chloro-2,4-diisocyanato-3,5,6-trifluorobenzene was found to be the diisocyanate; it yielded an adhesive system with the best overall properties.

This year, the various parameters influencing optimization of this system as a LOX-compatible adhesive were investigated.

Stringent quality control measures were found to be required. As a result, such methods were developed and utilized throughout the laboratory effort.

A standardized bonding procedure and a computer program were developed which assured consistent and reliable results. Consequently, the effect of compositional variables could be evaluated systematically.

Processing studies resulted in the production of the polyether of perfluoropropylene oxide in 4-pound batches, with improved yields of 37% of usable product. In addition, yields of 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene were increased to 70% in 1-pound runs.

The conditions necessary to prepare the isocyanate-terminated prepolymer of perfluoropropylene oxide were determined. A stabilizer was deemed unnecessary, and the prepolymer was found to be storage-stable for at least 6 weeks. A brief study of amine curing agents for this prepolymer failed to yield a satisfactory material.

Various parameters influencing the optimization of the fluorinated polyurethane adhesive were studied. Soluble iron, tin, and lead compounds were found to be effective catalysts, with iron resulting in the best overall properties at the 0.1% level. The pot life of this adhesive in small quantities was found to be 5 hours. The adhesive with iron, tin, or lead catalyst was found to be LOX compatible. The optimum adhesive cross-link density was at an NCO:OH ratio of 1.6:1.0, with little change up to a 2:1 ratio. The fluorinated polyurethane has excellent strength properties over the range from -320°F to +150°F. However, it is not recommended for use over +150°F.

## DISCUSSION

### QUALITY CONTROL

Previously, some difficulties were encountered with the fluorinated polyurethane from the perfluoropropylene oxide polyether and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene.\* Consequently, more stringent quality control measures were developed.

The quality control tests for the perfluoropropylene oxide polyether included molecular weight determination by vapor pressure osmometry (VPO) and hydroxyl content. The VPO determinations were made with a Mechrolab instrument; methyl ethyl ketone (MEK) was used as the solvent. The hydroxyl content was determined by using a modified acetylation technique, described in Appendix I.

Vapor phase chromatography (VPC) and isocyanate equivalency were found to be excellent quality control tests for 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene. The procedure for determining the isocyanate equivalency is described in Appendix II.

### STANDARDIZATION OF BONDING PROCEDURE

It was found that the existing bonding procedure was not adequate for obtaining consistent and valid test results. In some cases, the bondline thicknesses varied from 4 to 18 mils for the same set of bonds. In other cases, bond strengths varied from a low of 1620 psi to a high of 4120 psi within the same set of bonds. As a result, little confidence could be placed in the results obtained when adhesive variables were studied.

A brief study was conducted in an attempt to develop a standardized bonding procedure. Pressure was applied to the bonds by vacuum bagging. The test coupons were obtained from breakaway pads comprising eight test specimens. From the results of this study, the following conclusions were drawn:

1. The guide pins in the bonding fixture must be sufficiently loose to provide easy movement of the breakaway panels and to prevent binding of the panels on the pins.
2. No more than two breakaway panels should be stacked in each bonding fixture.
3. The fixture, doublers, shims and separators must be carefully inspected to ensure they are clean and smooth.
4. The end bonds in the fixture should not be used for testing.

---

\*Described in Summary Report V (1967) for this program.

In order to compare the effect of variables on adhesive performance, it was deemed necessary to compare data at the same bondline thickness. A computer program was developed for analyzing bondline - bond strength data to determine the best mean strength for 5-mil bondlines. The computer was programmed to:

1. Determine the mean tensile shear strength of the raw data.
2. Determine the mean tensile shear strength between 3- and 7-mil bondline thickness.
3. Determine the mean tensile shear strength at 5-mil bondline thickness obtained by a Least Squares analyses.
4. Determine a weighted average, based on the above calculations, and on previously obtained information about the adhesive system.
5. Compare this weighted average with other averages to determine whether a significant change has been made in the adhesive formulation. (These comparisons were made with the aid of a Student t confidence level of 95%).

To evaluate the new standardized bonding procedure, a series of bonds were made with the Baglbond 420 system described in Summary Report V. The data are listed in Table I.

These data showed there was no significant difference in bond strength when bonding was done either within 10 minutes or 4 hours after the coupons were removed from the drying oven. In addition, using a heat gun to apply the adhesive appeared to reduce the bond strength at room temperature. Finally, DC Z-6020 primer increased the bond strength of Baglbond 420. The new bonding procedure developed is included as Appendix III and the test method as Appendix IV.

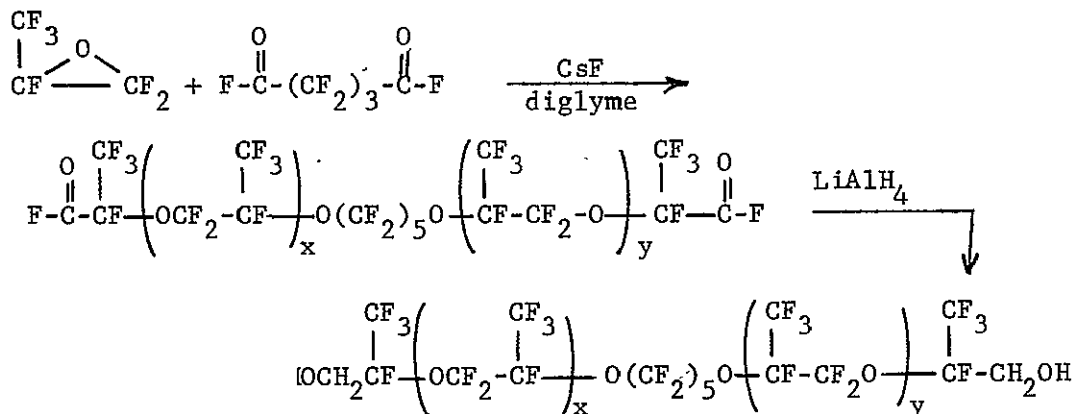
TABLE I

## EVALUATION OF THE STANDARDIZED BONDING PROCEDURE ON THE BAGLBOND 420 SYSTEM

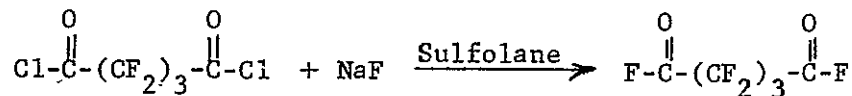
Tensile Shear Strength, psi			Remarks
-320°F	RT	+250°F	
3273	2171	176	Aluminum coupons left standing for 4 hours after etching and drying before bonding.
3206	1556	134	Aluminum coupons left standing for 4 hours after etching and drying before bonding -- coupons heated with heat gun during bonding.
4142	2925	227	Aluminum coupons left standing for 4 hours after etching and drying before bonding -- panels primed with DC Z-6020 primer.
3595	2182	154	Bonds made within 10 minutes after removal from drying oven.

PROCESS STUDIES

Efforts were made to lower the cost and improve both yield and purity of the hydroxyl-terminated polyether of perfluoropropylene oxide. The data obtained would also be used to determine the manufacturing procedures required to produce the material on a large scale. This polyether is prepared as follows:



The perfluoroglutaryl fluoride was prepared in an overall yield of 80% as follows:



This reaction is straightforward, and pilot runs provided over 2 pounds of product per run. Larger scale production of this material should pose no problem.

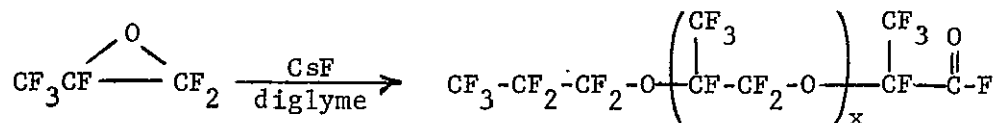
In the preparation of the acid fluoride-terminated polyether, the effect of reaction temperature was studied since it is one of the most important variables affecting the yield and molecular weight of the product. The results of this study are listed in Table II.

TABLE II

EFFECT OF REACTION TEMPERATURE ON YIELD OF ACID FLUORIDE  
TERMINATED POLYETHER OF PERFLUOROPROPYLENE OXIDE

Run No.	Reaction Temp, °C	Total Yield of Fluorocarbon Products, %	Yield of Usable Polyether, %
2097-20	0-30	85	29
2119-31	15-16	--	45
2119-18	9-11	--	48
2119-40	0	--	46

As shown, lower temperatures are conducive to higher yields of usable product. In addition, approximately 50% of all fluorocarbon products cannot be used since they are monofunctional materials, formed by the homopolymerization of perfluoropropylene oxide in the following manner:



The acid fluoride terminated polyether is reduced directly to the diol in virtually quantitative yield by using lithium aluminum hydride. The hydroxyl-terminated polyether is then distilled to remove any remaining monofunctional products as well as the extremely high molecular weight materials. Table III lists the overall conversion of the various runs of polyether from Table II. Table III shows that the optimum yield of 37% usable product is obtained when the polymerization is conducted at a 10°C.

TABLE III  
SUMMARY OF RESULTS FROM THE PREPARATIONS OF THE  
HYDROXYL-TERMINATED POLYETHER OF PERFLUOROPROPYLENE OXIDE

Run No.	Polymerization Temp, °C	Run No. of Starting Material	Overall Yield of Product, %	Product Molecular Weight
2097-21	0-30	2097-20	25	1100
2119-38	15-16	2119-31	28-1/2	1500
2119-24	9-11	2119-18	37	1700
2132-1-D	0	2119-40	34	1500

The polyether preparation was scaled up to the point where 4 pounds are now being produced in each run.

Process and scale-up studies were also conducted on 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene. As shown in Table IV, yields improved when the phosgenation had been run within the range from -10°C to +10°C. The reaction is essentially complete after 2 hours (see Table V). This reaction was successfully scaled-up to produce 1 pound per run at a yield of 70%.

TABLE IV

EFFECT OF REACTION TEMPERATURE ON THE YIELD OF  
1-CHLORO-2,4-DIISOCYANATO-3,5,6-TRIFLUOROBENZENE

Reaction Temp, °C	Reaction Time, hr	% Yield
≈ -78	4.0	42
≈ -78	3.5	36
-10 to 0	4.5	69
-10 to +10	2.0	70

TABLE V

EFFECT OF TIME ON THE REACTION RATE OF PHOSGENATION  
OF THE 1-CHLORO-2,4-DIAMINO-3,5,6-TRIFLUOROBENZENE

Time, hr	Weight of Crude Product/ 100 ml	Relative Amount of Product (by VPC)	Description of Crude Product
0*	2.57	--	Solid
0**	3.14	30	Solid + cloudy liquid
1/4	4.25	33	Paste
1	4.72	45	Paste
2	3.88	44.5	Cloudy liquid
4	4.50	41	Clear liquid + solid
22	(≈4.0)	(≈40)	Clear liquid + solid

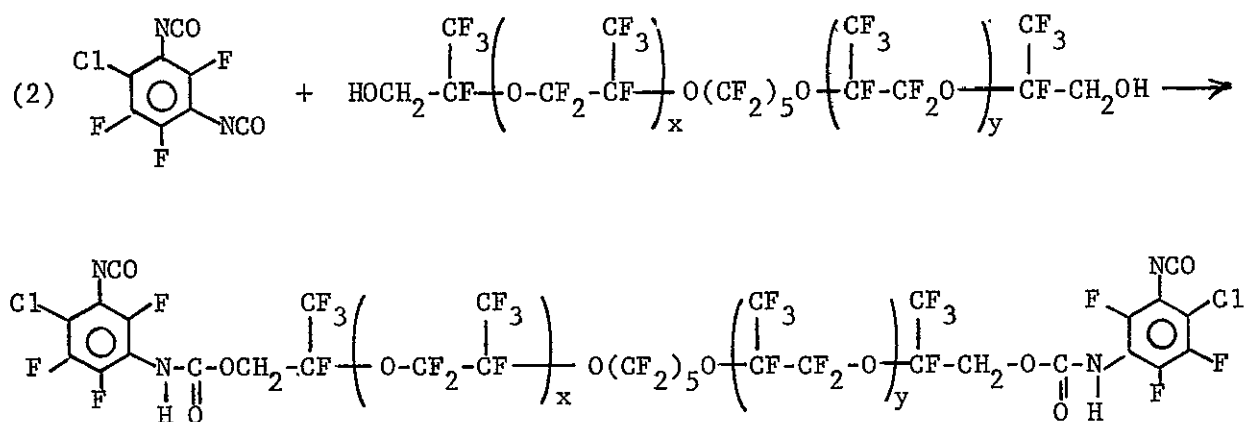
\*50% of amine added to reaction.

\*\*100% of amine added to reaction (Time = 0).



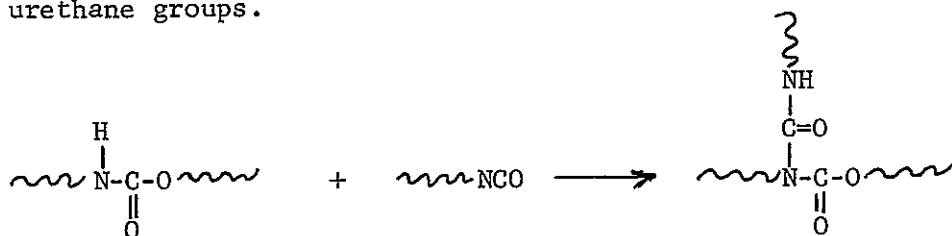
## ISOCYANATE-TERMINATED PREPOLYMERS

In order to reduce any possible toxicity hazard associated with the use of diisocyanate monomer, a study was conducted into the preparation of the isocyanate-terminated prepolymer shown below:

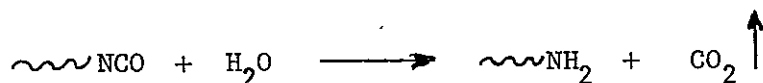


The reaction of the diisocyanate with the polyether of perfluoropropylene oxide was followed by infrared analysis. Initially, the diisocyanate is insoluble in the polyether, but dissolves as it reacts. It was determined that a period of 2 hours at 80°-100°C is required to complete the reaction when conducted in the melt. The final product is a semi-solid at room temperature, but a viscous liquid at 60°-70°C.

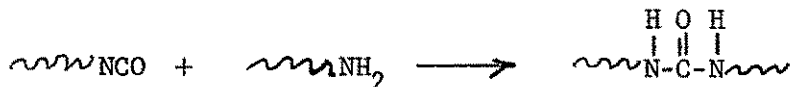
A number of undesirable side reactions which would result in branching can occur during the preparation of the isocyanate-terminated prepolymer. For example, allophanate groups are formed by the reaction of isocyanate and urethane groups.



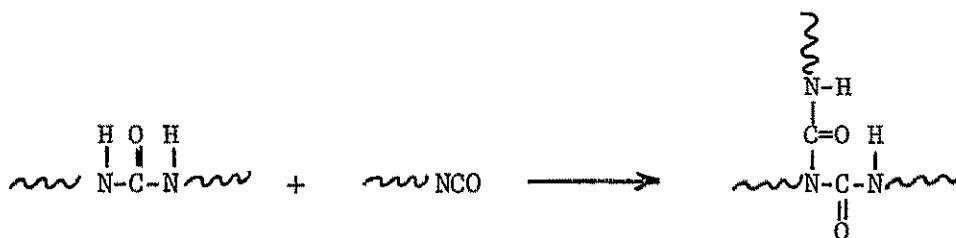
Traces of water react with isocyanates to form amines,



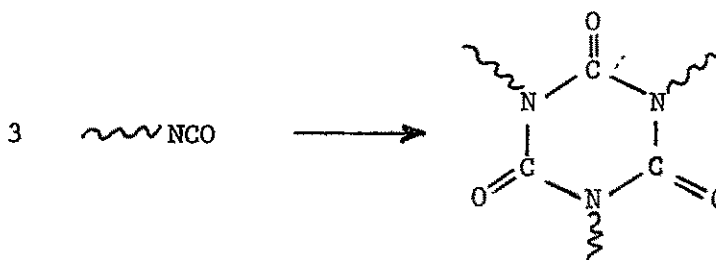
which then react with additional isocyanate groups to form ureas.



Biuret groups are then formed by the reaction of isocyanate and urea groups.



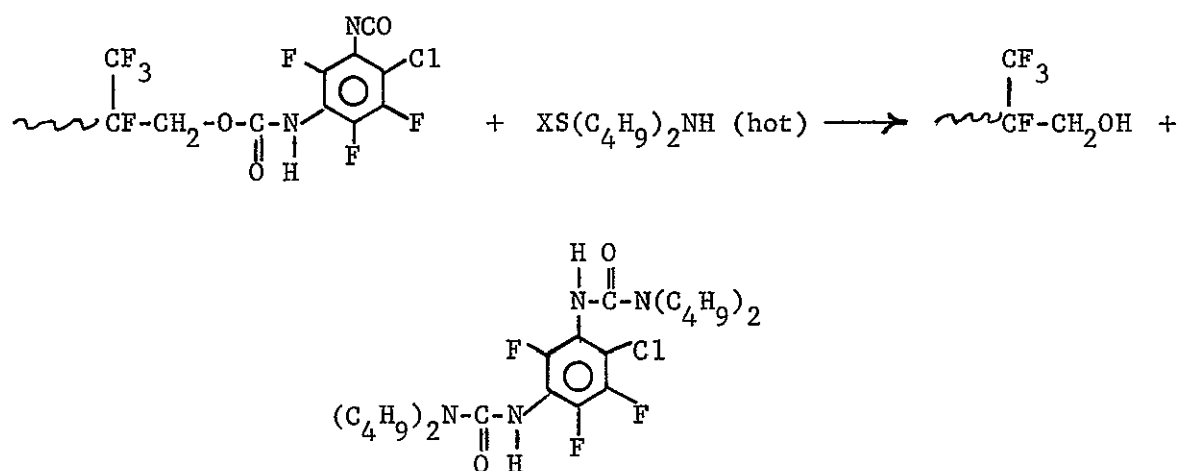
Trimerization can also occur from the reaction of three isocyanate end groups.



Normally, all of these side reactions can be minimized by preparing the prepolymer in an acidic system at temperatures of 100°C or less. With conventional polyurethanes, the acidity is controlled by the incorporation of 0.03% benzoyl chloride, or phthaloyl chloride or hydrogen chloride.

The isocyanate-terminated prepolymer described above was prepared in an acidic system by using benzoyl chloride. It was found that the viscosity of the prepolymer was significantly less than that prepared without benzoyl chloride. This indicated some or all of the undesirable side reactions occur unless the reaction is conducted in an acidic medium. Since the prepolymer was a semisolid at room temperature, it was necessary to add 13% free 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene in order to reduce the viscosity to a workable level. This prepolymer was stable for 1 week at room temperature in a capped bottle. However, after 11 days, a white crystalline solid formed on the surface of the prepolymer. Apparently sufficient moisture had diffused through the cap of the bottle to hydrolyze the isocyanate groups on the prepolymer surface. The prepolymer requires storage in a container with a desiccant to prevent hydrolysis.

The isocyanate equivalency analysis, described in Appendix II, was found to be unsatisfactory as a quality control test for determining the free isocyanate content of the isocyanate-terminated prepolymer of perfluoropropylene oxide. In this test, the sample is reacted with excess dibutyl amine at reflux to assure complete reaction of all isocyanate groups. With the isocyanate-terminated prepolymer, however, the hot dibutyl amine apparently attacks the urethane groups in the prepolymer as well as the free isocyanate groups, resulting in an excessively high isocyanate content.



Consequently, a new procedure was devised for determining the free isocyanate content of the isocyanate-terminated prepolymer of perfluoropropylene oxide. This procedure is attached as Appendix V.

The new prepolymer system (containing benzoyl chloride stabilizer) was evaluated in an adhesive formulation. The standardized bonding method described previously was used. In addition, several primers were given a preliminary screening. Test results are presented in Table VI.

TABLE VI

VALUATION OF THE FLUORINATED POLYURETHANE ADHESIVE  
FROM ISOCYANATE-TERMINATED PREPOLYMER AND PRIMERS

Tensile Shear Strength, psi			Remarks
-320°F	RT	+250°F	
1246	739	87	Control
2241	1645	94	DC Z-6020 primer
1521	1219	56	DC Z-6040 primer
1655	1252	43	DC C-600 primer

The above data indicate that:

1. The use of Z-6020 primer improves the bond strength of the fluorinated adhesive at both -320°F and room temperature, reaffirming data obtained previously.
2. Z-6040 and C-600 primers have little effect on strength at room temperature, but strengths at -320°F are improved.
3. The fluorinated adhesive had a disappointingly low bond strength. The benzoyl chloride stabilizer may be poisoning the catalyst, or the cure cycle may be inadequate.

To determine whether or not excess benzoyl chloride was deleterious, we compared the fluorinated adhesive bond strength without benzoyl chloride and with 0.3% benzoyl chloride (see Table VII).

TABLE VII

EFFECT OF BENZOYL CHLORIDE ON BOND STRENGTH  
OF THE FLUORINATED ADHESIVE

Tensile Shear Strength, psi			Remarks
-320°F	RT	+250°F	
3262	2113	172	No benzoyl chloride
1291	764	60	0.3% benzoyl chloride based on total adhesive composition

As shown in this table, the use of benzoyl chloride at the 0.3% level drastically reduces the bond strength of the adhesive.

Up to this point, polyether of 1100 molecular weight was used. A new run was made with a polyether having a molecular weight of 1700. All subsequent evaluations described in this report were based on this polyether. Since this polyether had a higher molecular weight than that used previously, lower bond strengths were expected.

To learn more about the influence of benzoyl chloride on bond strengths of the fluorinated polyurethane adhesive, we conducted a brief study to determine the effect of extremely low concentrations of benzoyl chloride. The isocyanate-terminated prepolymer used was prepared from the recent run of polyether. The results are shown in Table VIII

TABLE VIII

EFFECT OF VARYING CONCENTRATIONS OF BENZOYL CHLORIDE ON  
BOND STRENGTH OF THE FLUORINATED POLYURETHANE ADHESIVE

Tensile Shear Strength, psi			% Benzoyl Chloride	Isocyanate-Terminated Prepolymer Viscosity at 60°C, seconds*
-320°F	RT	+200°F		
1674	1210	--	None	19.2
2556	1544	118	0.06	16.2
1846	1412	148	0.03	14.2

\* Gardner-Holt viscosity.

These data implied that, while 0.03% benzoyl chloride gives a prepolymer with a lower viscosity, there is no significant improvement in strength properties. Furthermore, the use of 0.06% benzoyl chloride appears to improve bond strengths. However, since 1% stannous octoate was used as a catalyst, this concentration may be excessive and the higher concentration of benzoyl chloride is nullifying the effect of the excess catalyst.

In order to evaluate the necessity of using benzoyl chloride to provide adequate storage stability, a sample of the prepolymer was made without benzoyl chloride. It was stored for 6 weeks in a container having a dessiccant. A fluorinated polyurethane adhesive was prepared from this

prepolymer before and after storage. The results in Table IX show the isocyanate-terminated prepolymer is stable for at least 6 weeks if properly stored. In addition, benzoyl chloride is not necessary to provide storage stability of the prepolymer. The short duration of this contract precluded more extensive evaluation of shelf stability.

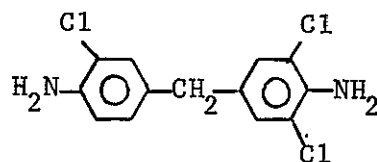
TABLE IX

EFFECT OF STORAGE OF THE ISOCYANATE-TERMINATED PREPOLYMER ON BOND STRENGTHS OF THE FLUORINATED POLYURETHANE ADHESIVE

Tensile Shear Strength, psi			Remarks
-320°F	RT	+200°F	
4802	1360	142	Control
4467	1548	140	Isocyanate-terminated prepolymer stored for 6 weeks

#### CURING AGENTS

Curalon L, shown below, was evaluated and was found to be unsatisfactory as a curing agent for the isocyanate-terminated prepolymer prepared previously. As soon as the first drop of Curalon L was added, the prepolymer gelled into a heterogeneous solid mass.



"Curalon L"

An attempt to prepare a mixed curing agent of Curalon L and the hydroxyl-terminated polyether of perfluoropropylene oxide was not successful. Curalon L is insoluble in the polyether and crystallizes when the mixture cools.

This brief effort at utilizing amines as a curing agent for the isocyanate-terminated prepolymer was unsuccessful. However, amines typically result in polyurethanes with marked improvement in physical

properties over diol cured systems. Therefore, if a LOX compatible amine curing agent could be developed, a sizable improvement in adhesive characteristics could be expected.

#### ADHESIVE OPTIMIZATION

Since 250°F is in excess of the expected operating temperature requirement for this type of adhesive, high-temperature tensile shear strengths were determined at a maximum temperature of 200°F.

#### Catalyst Study

A number of soluble metallic compounds are available that catalyze the urethane and allophanate reactions. To evaluate the effect of these materials on the fluorinated polyurethane system, a group was selected which covers a broad spectrum of relative reactivities. The catalysts evaluated were soluble salts of iron, lead, manganese, tin, copper, and cobalt. These were screened at two concentration levels, 0.1% and 1.0%. The results of this preliminary evaluation (Tables X and XI) show that excess catalyst drastically reduced the bond strength of the adhesive. While all catalysts were effective in the adhesive system, results for manganese, copper and cobalt were somewhat inferior to those for the other catalysts evaluated.

TABLE X

SCREENING OF CATALYSTS IN THE FLUORINATED POLYURETHANE ADHESIVE  
(0.1% METAL CATALYST CONCENTRATION)

Catalyst*	Pot Life @ RT, hr	Gel Time @ 160°F, min	Tensile Shear Strength, psi	
			-320°F	RT
Iron	5 1/2	28	4802	1360
Lead	3 1/2	2.3	3685	1220
Tin	0	5.6	4073	1730
Manganese	>6 1/2	53	1531	965
Copper	>5 1/2	36	3620	827
Cobalt	>5 1/2	6.8	3726	906
None	--	88	--	--

\* As soluble metal salts of organic acids.

TABLE XI

SCREENING OF CATALYSTS IN THE FLUORINATED POLYURETHANE ADHESIVE  
(1.0% METAL CATALYST CONCENTRATION)

Catalyst	Gel Time @ 160°F, min	Tensile Shear Strength, psi	
		-320°F	RT
Iron	9.5	1429	691
Lead	1.9	3048	1430
Tin	2.5	356	1006
Manganese	15	194	115
Copper	14.6	770	618
Cobalt	1.5	440	495
None	88	--	--

The results of the preliminary screening evaluation pointed out that iron, lead, and tin should be selected for further study. These catalysts were examined over a range of concentrations in order to select the optimum catalyst and concentration, to maximize tensile shear strength, and to obtain the maximum workable pot life.

As shown in Table XII and Figure 1, the effect of catalyst concentration on gel time produced the expected linear relationship. The adhesive was more sensitive to varying concentrations of lead than to either one of the other catalysts. Under the same conditions, a gel time of a typical commercial two-component polyurethane adhesive is 32 minutes.\*

It should be pointed out that great latitude in curing rates is possible through relatively small variations in catalyst concentration. Almost any gel time can be obtained, depending on the particular requirements of the adhesive system. A point worth mentioning is that the use of metal equipment or containers would almost certainly negate shelf life.

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\*Narmco 7343.



TABLE XII  
EFFECT OF CATALYST CONCENTRATION ON GEL TIMES

Catalyst	Concentration, %	Gel Time at 160°F, min
Lead	0.02	28.0
	0.05	11.5
	0.10	8.6
	0.30	3.4
	1.00	1.9
Iron	0.02	43.0
	0.05	21.0
	0.10	28.0
	0.30	14.0
	1.00	9.5
Tin	0.003	22.0
	0.01	13.1
	0.03	7.1
	0.10	4.4
	1.0	2.5
None	--	88.0

Bonds were made with the fluorinated polyurethane adhesive and the tin, lead, or iron catalyst at several concentrations. Resulting data are shown in Table XIII and are graphically reproduced in Figures 2 through 4.

The optimum concentration of tin catalyst appears to be 0.01%. However, this catalyst demonstrated both extreme sensitivity to gelation and a short pot life. Consequently, this catalyst was not studied further at this time.

Iron catalyst or lead catalyst gave optimum results at the 0.1% concentration level, with iron giving significantly better results at -320°F. In all cases, however, excess catalyst seriously reduced the bond strength at -320°F, with little apparent effect on the room temperature results. All bonds had poor strengths at +200°F. In addition, both catalysts exhibited good pot life, and they were comparable to conventional two-component polyurethane adhesive systems.

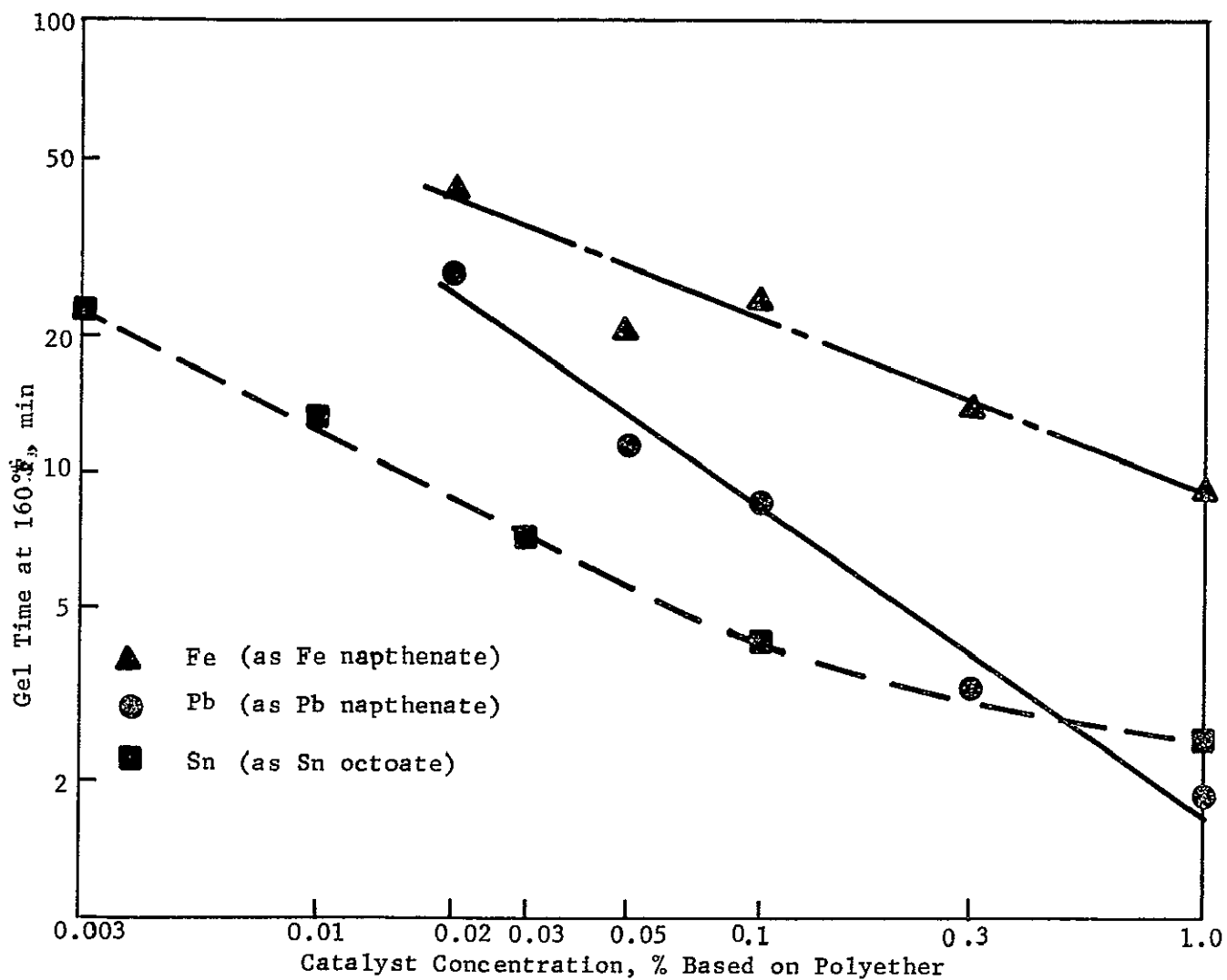


Figure 1. Gel Times at 160°F for Various Catalyst Concentrations

TABLE XIII

EFFECT OF CATALYST CONCENTRATION ON BOND STRENGTH  
OF THE FLUORINATED POLYURETHANE ADHESIVE

Catalyst Concentration, %	Pot Life @ RT, hr	Tensile Shear Strength, psi		
		-320°F	RT	+200°F
IRON CATALYST				
0.02	>3	2032	792	105
0.05	>2	2528	742	98
0.10	5-1/2	5379	1360	142
0.30	>2	3718	909	83
1.00	--	1429	691	--
LEAD CATALYST				
0.02	>7-1/2	2755	992	118
0.05	6-1/2	4227	1037	88
0.10	3-1/2	4228	1215	104
0.30	2	3034	1250	118
1.00	--	3048	1430	--
TIN CATALYST				
0.003	>5-1/2	4508	1273	130
0.01	1	4906	1527	160
0.03	1/6	4030	1220	154
0.10	--	3153	1430	194
1.00	--	356	1006	25

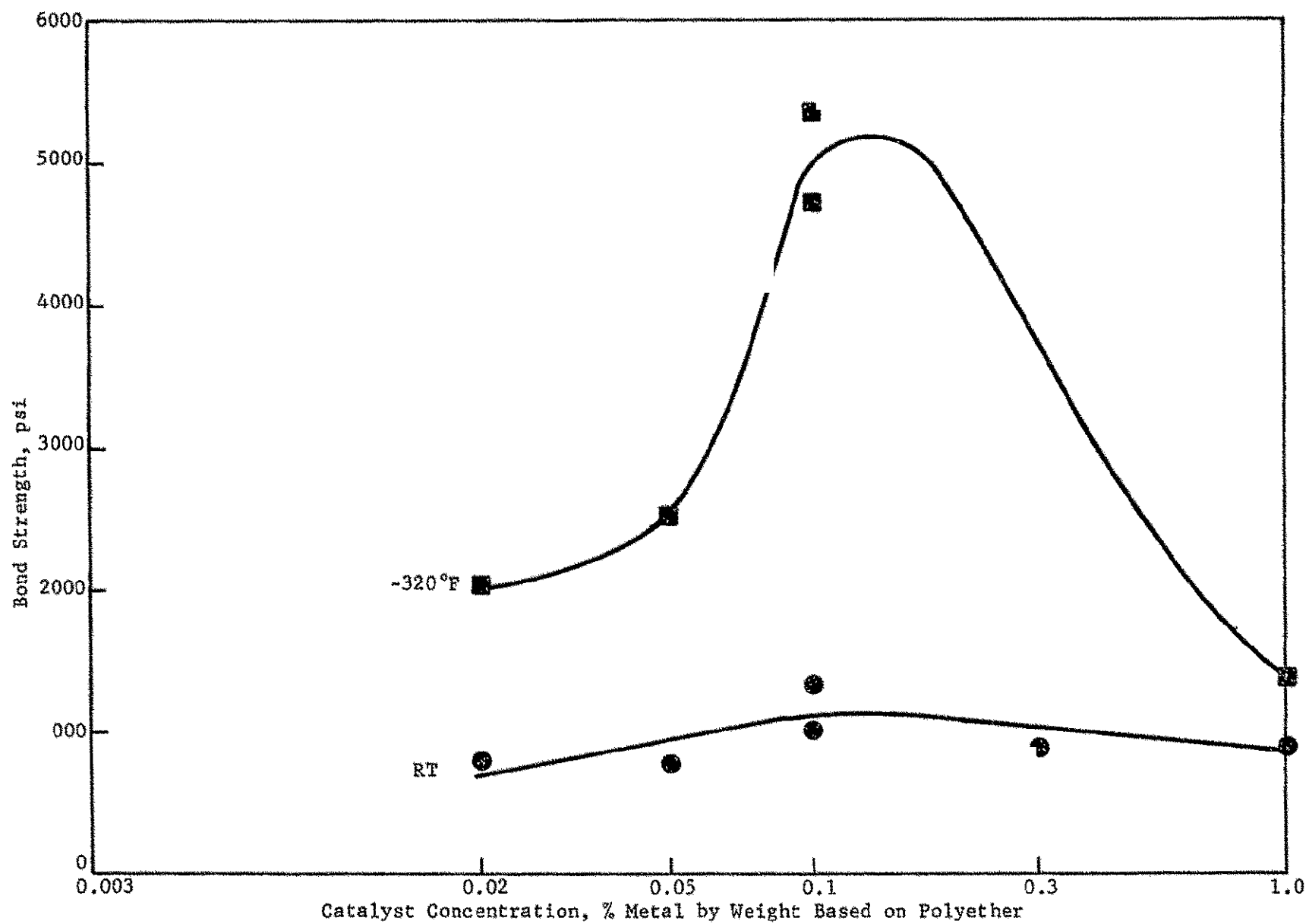


Figure 2. Effect of Iron Catalyst Concentration on Bond Strength<sup>h</sup>

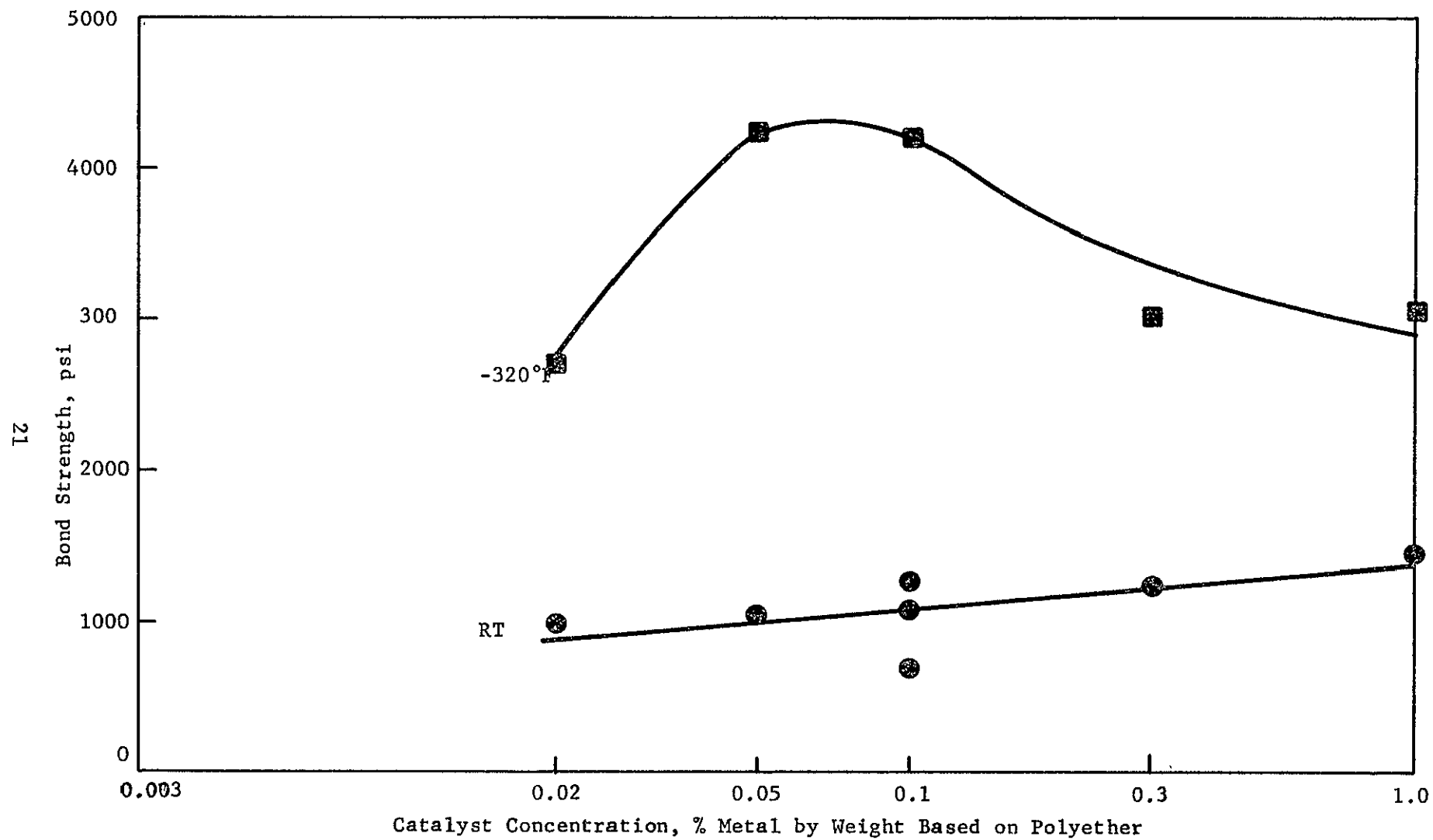


Figure 3. Effect of Lead Catalyst Concentration on Bond Strength

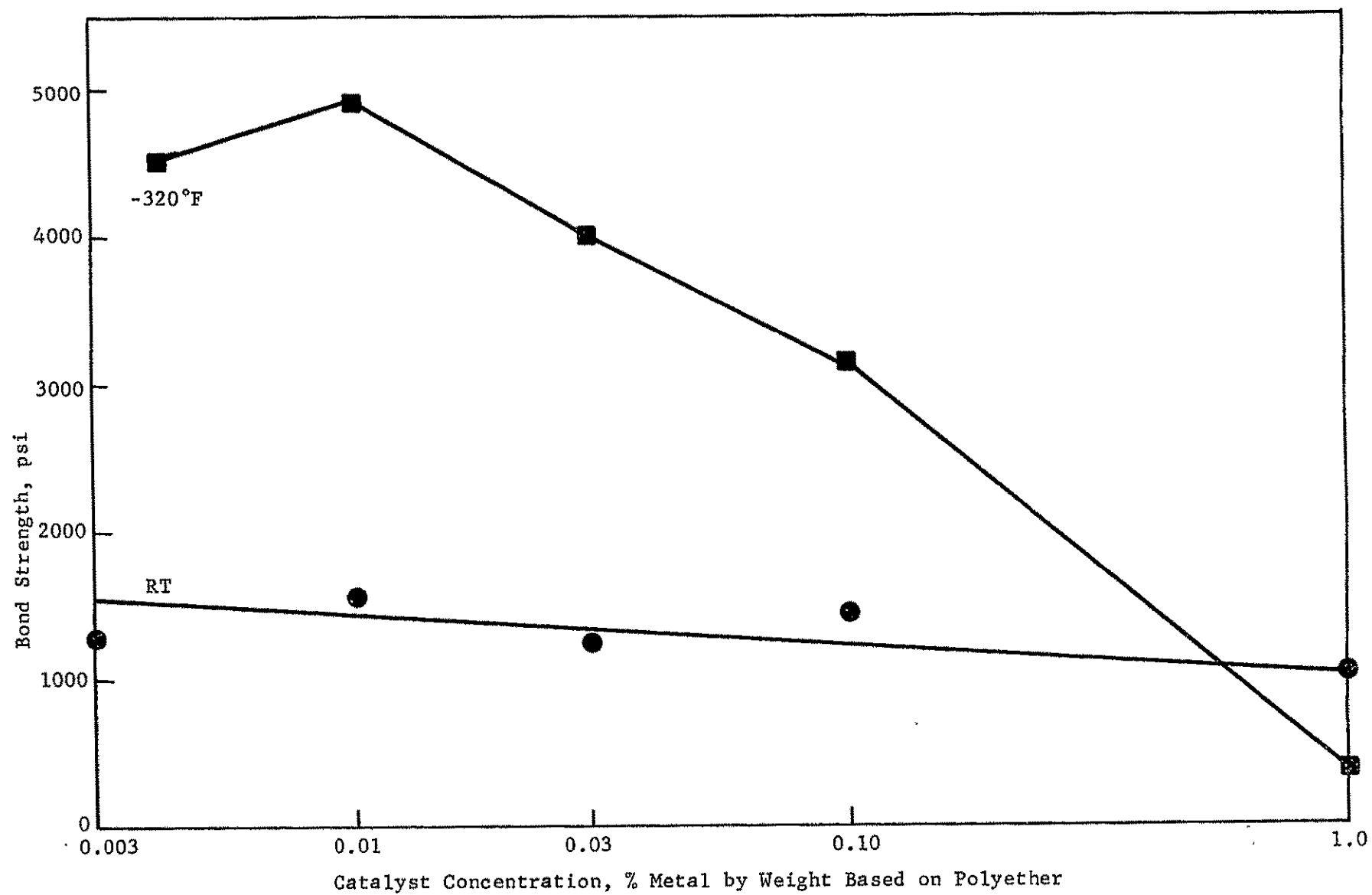


Figure 4. Effect of Tin Catalyst Concentration on Bond Strength

The effect of several curing conditions on each of the three most promising catalysts was studied. As shown in Table XIV, adhesive properties decreased when cured at 200°F. However, the bond strength increased when cured for 48 hours at 160°F without vacuum bagging. This improvement was attributed to a lesser amount of bubbles present in the bondline as a result of the vacuum bagging operation.

TABLE XIV  
EFFECT OF CURE CONDITIONS ON BOND STRENGTHS OF  
THE FLUORINATED POLYURETHANE ADHESIVE

Catalyst	Curing Conditions*	Tensile Shear Strength, psi		
		-320°F	RT	+200°F
0.1% Lead	A	4228	1215	104
	B	3637	795	84
	C	5075	1337	177
0.1% Iron	A	5379	1360	142
	B	2453	813	102
	C	5920	1259	139
0.1% Tin	A	3153	1430	194
	B	3908	1181	155
	C	4549	1707	198

\* A Overnight in vacuum bag @ 7.5 psi and RT, plus 48-hr postcure at 160°F.

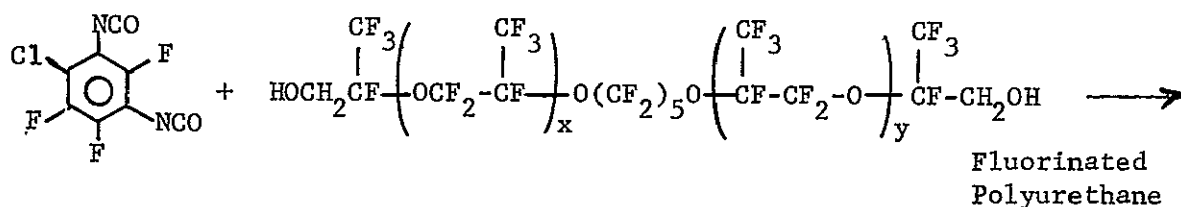
B Overnight in vacuum bag @ 7.5 psi and RT, plus 48-hr postcure at 200°F.

C 48-hr cure in oven at 160°F.

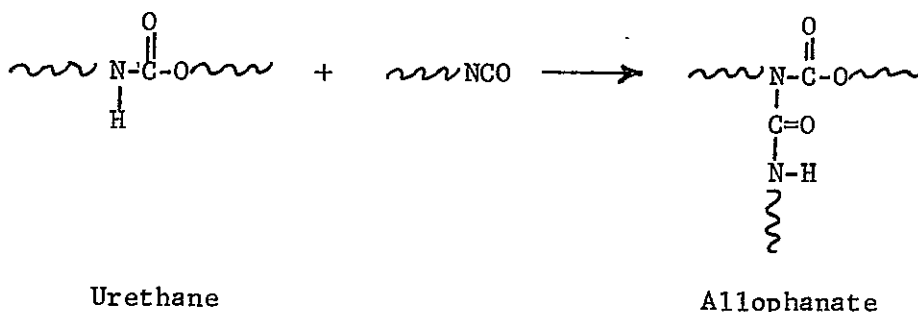
Each of the three most promising catalysts were used in samples of the fluorinated polyurethane submitted to NASA-Huntsville for LOX compatibility. These included 0.1% iron, 0.1% lead, and 0.01% tin. There was no reaction in any of the 60 specimens tested. The evidence indicated this polymer is LOX compatible.

### Effect of Cross-link Density

The fluorinated polyurethane is prepared by reaction of the hydroxyl-terminated polyether of perfluoropropylene oxide and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene, as follows:



Crosslinking is achieved by using excess diisocyanate, which reacts with the urethane groups to form allophanate crosslinks.



Crosslink density is controlled by the NCO:OH ratio. As the NCO:OH ratio increases, the crosslink density increases.

A study was conducted to determine the effect of crosslink density on bond strength of the fluorinated polyurethane adhesive. The effect of NCO:OH ratio over the range from 1:1 to 2:1 was investigated. Results are presented in Table XV and Figure 5. The prepolymer contained no benzoyl chloride, and the adhesive had 0.1% iron catalyst as iron naphthenate.

As shown in Figure 5, the bond strength of the fluorinated polyurethane adhesive increased rapidly from an NCO:OH ratio of 1:1 to 1.6:1, after which the strength remained essentially the same. All bond strengths above an NCO:OH ratio of 1.4:1 were excellent at both -320°F and room temperature.

### Temperature-Adhesive Strength Profile

The effect of temperature on the adhesive strength of the fluorinated polyurethane was studied in order to define its applicable temperature range. Such data were also required for engineering design purposes. The adhesive was the optimum formulation developed to date, containing 0.1% iron catalyst at an NCO:OH ratio of 1.8:1.



TABLE XV

EFFECT OF CROSSLINK DENSITY ON BOND STRENGTH  
OF THE FLUORINATED POLYURETHANE ADHESIVE

NCO:OH Ratio	Gel Time, min	No. Specimens	Test Temp, °F	Tensile Shear Strength, psi
1.0:1	119	3	-320	9
		3	RT	10.5
		3	+200	0
1.2:1	60	3	-320	19
		3	RT	52
		3	+200	0
1.4:1	20	4	-320	2355
		4	RT	1156
		8	+200	79
1.6:1	25	4	-320	5280
		4	RT	1880
		6	+200	111
1.8:1	17	4	-320	5175
		4	RT	1738
		8	+200	155
2.0:1	41	4	-320	5229
		4	RT	1567
		8	+200	174

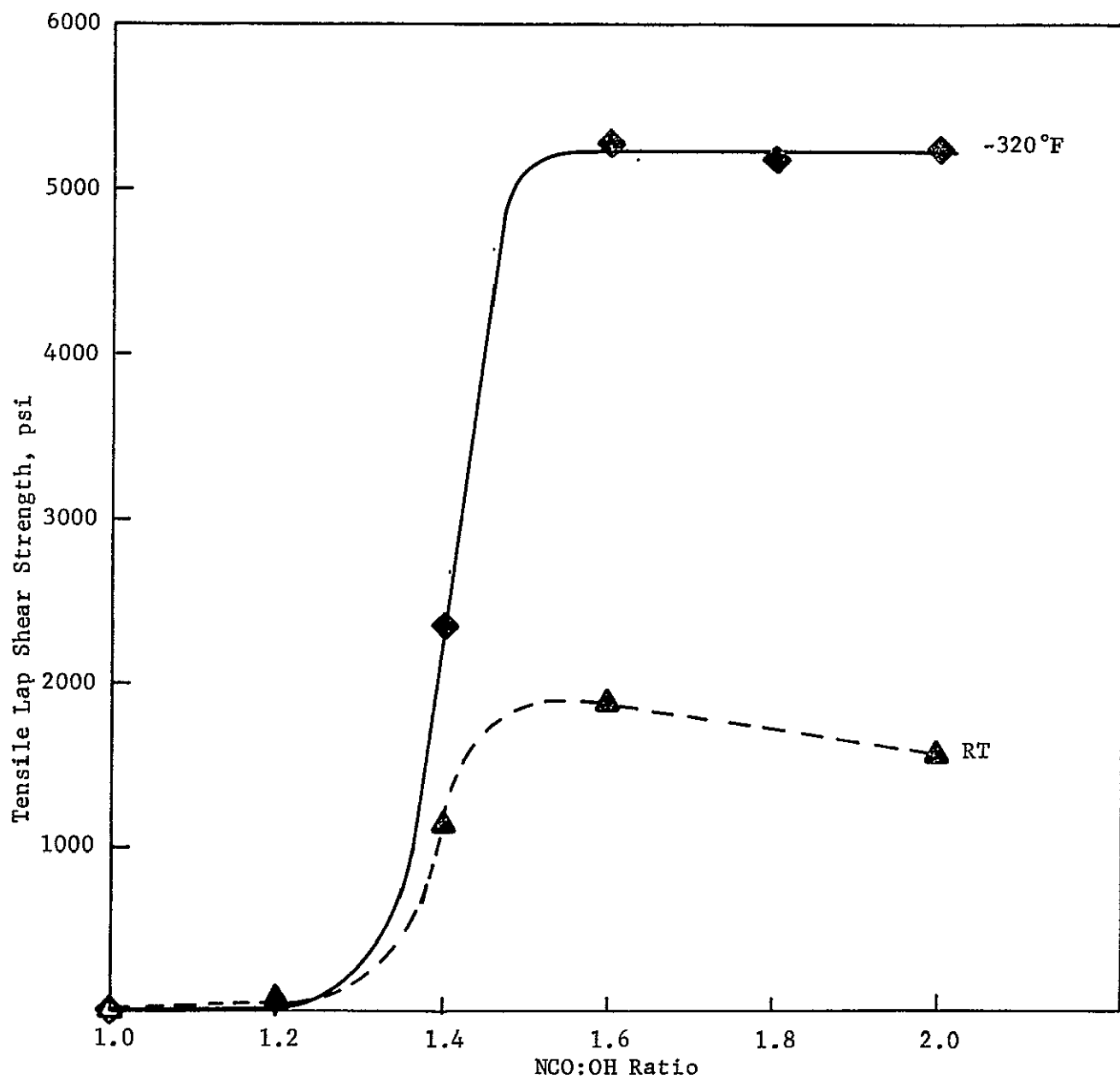


Figure 5. Effect of NCO:OH Ratio on Bond Strength of the Fluorinated Polyurethane Adhesive

As the test data in Figure 6 indicated, this adhesive has good properties over the temperature range from -320°F to +150°F. However, it is not considered to be acceptable at temperatures in excess of +150°F.

#### Effect of Fillers

Titanium dioxide ( $\text{TiO}_2$ ) was selected as a typical filler and given a preliminary evaluation to determine its effect on the fluorinated polyurethane adhesive. As shown in Table XVI, the addition of more than 20-phr titanium dioxide as a filler seriously lowered the adhesive strength of the fluorinated polyurethane. At lower concentrations, its effects was inconclusive. It is believed that a more complete screening and evaluation of fillers is required.

TABLE XVI

#### EFFECT OF TITANIUM DIOXIDE FILLER ON ADHESIVE PROPERTIES OF THE FLUORINATED POLYURETHANE

$\text{TiO}_2$ , phr <sup>2</sup>	Gel Time @ 160°F, min	Tensile Shear Strength, psi		
		-320°F	RT	+200°F
0	23	2128	1138	88
10	37	2814	1098	132
20	28	4479	933	156
30	18	80	500	33
40	16	210	373	130
50	11	49	411	43

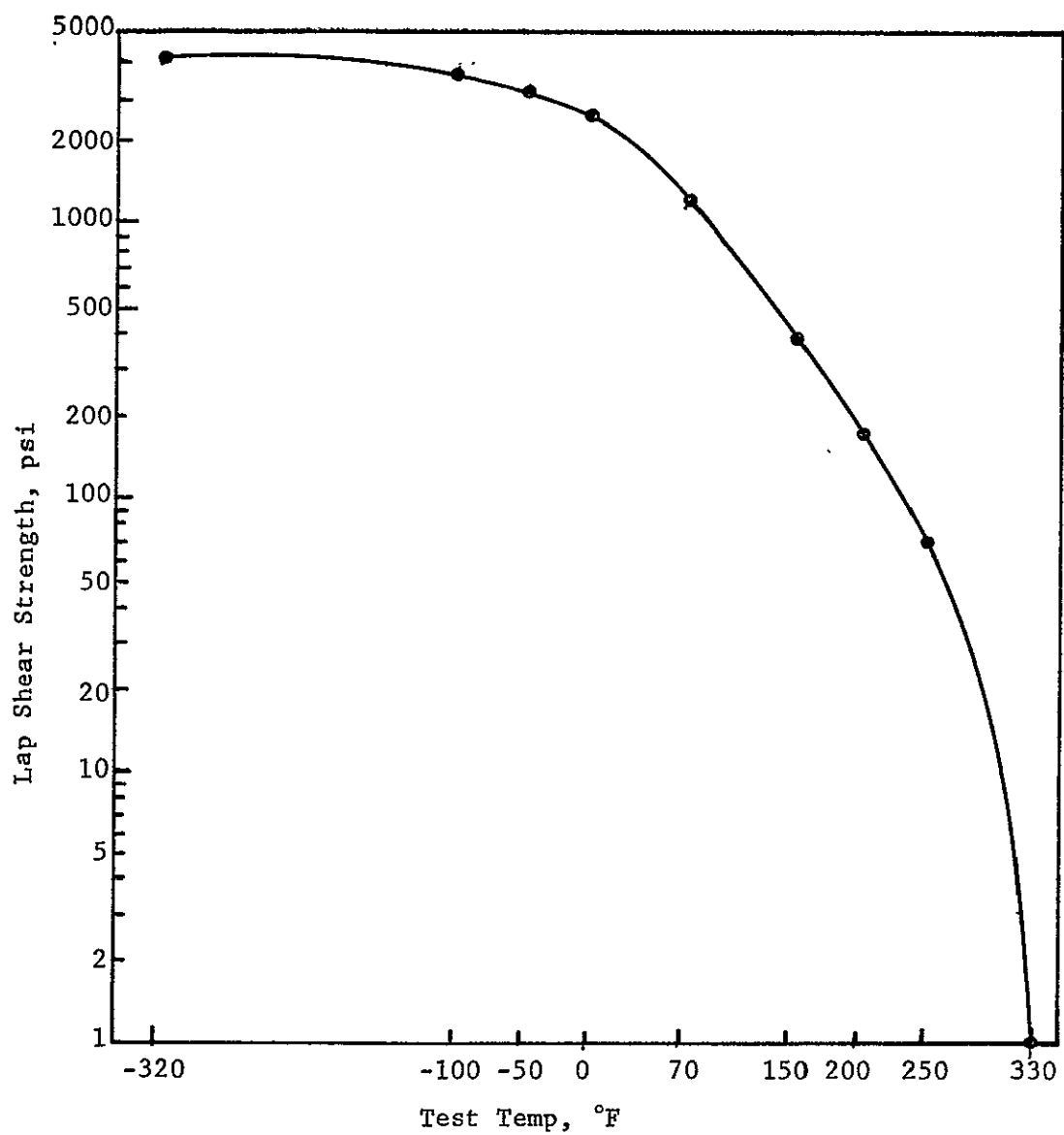


Figure 6. Temperature-Strength Profile of the Fluorinated Polyurethane

## EXPERIMENTAL

### PREPOLYMER PREPARATION

A typical procedure for the preparation of the isocyanate-terminated prepolymer of perfluoropropylene oxide follows. The hydroxyl-terminated prepolymer of perfluoropropylene oxide having a molecular weight of 1100 (11.00 g, 0.01 mole) is charged to a reaction vessel previously purged with nitrogen. 1-Chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (4.98 g, 0.02 mole) is added and the mixture is stirred for 20 minutes at 60°-80°C, then held for 1 hour and 40 minutes at 80°-100°C under a blanket of nitrogen. It is then cooled to 70°C and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene (2.48 g, 0.01 mole) is added, with stirring. The prepolymer is kept in a capped bottle in a desiccator.

### PROCESS STUDIES

#### Perfluoroglutaryl Fluoride

The following is a typical preparation of perfluoroglutaryl fluoride. Sodium fluoride (366 g, 8.7 mole) is dried for 48 hours at 600°F, then slurried in redistilled sulfolane (1050 ml). Perfluoroglutaryl chloride (664 g, 2.4 mole) is added to the slurry at 35°-40°C over a 2-hour period. The mixture is then refluxed for 3 hours and distilled.

This procedure yielded 467 g of perfluoroglutaryl fluoride (80% yield) of 99%+ purity.

#### Acid-Fluoride-Terminated Polyether of Perfluoropropylene Oxide

The typical conditions for the preparation of this product consist of the following. Redistilled diglyme (250 ml) is added to cesium fluoride (66.9 g, 0.44 mole) which has been dried at 600°F for 3 days. Perfluoroglutaryl fluoride (173.2 g, 0.7 mole) is added to this slurry over a 1-hour period; during this time the temperature is maintained at 15°-20°C. The mixture is cooled to -25°C, and perfluoropropylene oxide (50 g) is added. The slurry is heated to 20°-25°C, then cooled to 15°-16°C. Perfluoropropylene oxide (1450 g) is added over a 4-hour period, with the temperature maintained at 15°-16°C. The product is allowed to stand overnight and the cesium fluoride is then filtered off. The product is decanted and distilled. All fluorocarbon products boiling above 77°C at 1.5 mm are removed, yielding 753.4 g of product.

#### Hydroxyl-Terminated Polyether of Perfluoropropylene Oxide

Lithium aluminum hydride (50 g, 1.3 mole) is suspended in 2500 ml of dry tetrahydrofuran. The acid fluoride terminated polyether of perfluoropropylene oxide (753.4 g) is added to the lithium aluminum hydride slurry over a 1-hour period at 25°-35°C. It is mixed for an additional 3-1/2 hours at 30°-35°C, then a mixture of tetrahydrofuran (250 ml) and water (180 ml) is added over a 1-1/2 hour period at 30°-35°C. The mixture is poured into 5% sulfuric acid (10 l) and left standing overnight. The product is decanted and vacuum-distilled.

With this procedure, the product that was collected boiled from 85°C to 160°C at 0.5 mm (478.4 g). The molecular weight by vapor pressure osmometry in methyl ethyl ketone was 1470, and the hydroxyl content was 2.16%.

#### 1-Chloro-2,4-diisocyanato-3,5,6-trifluorobenzene

Dry ether is cooled to -10 to 0°C, and liquid phosgene (450 g, 4.6 mole) is added below the surface of the ether solution over a period of 15 minutes. To this solution is added pyridine (320 g, 4.1 mole) over a 45-minute period, then 1-chloro-2,4-diamino-3,5,6-trifluorobenzene (196.5 g, 1 mole) dissolved in ether (750 ml) is added over a period of 1.5 hours. The solution is allowed to warm to room temperature over a 4- to 5-hour period. The white solids are filtered off and washed with anhydrous ether (1 l), and the combined liquid is concentrated on a rotating evaporator, followed by vacuum distillation.

With this procedure, the product was obtained in 70% yield (168 g) (bp 102°-103°C at 3.5-4.0 mm).

## CONCLUSIONS

Stringent quality control measures must be performed on all monomers and prepolymers used on this program.

A standardized bonding procedure is required in order to obtain a uniform bondline thickness and reliable test data. In bonding aluminum coupons, the panels can be bonded for up to 4 hours after removal from the oven after etching; primers have indicated a technique to significantly improve bond strengths. The most impressive results were obtained with Dow-Corning Z-6020 primer.

1-Chloro-2,4-diisocyanato-3,5,6-trifluorobenzene can be prepared in 70% yield and in quantities up to 1 pound per run. The hydroxyl-terminated polyether of perfluoropropylene oxide can be produced in batch sizes up to 4 pounds per run with an overall yield of 37% based on starting materials.

In preparing the isocyanate-terminated prepolymer of the polyether of perfluoropropylene oxide, an acidic stabilizer such as benzoyl chloride is not required. The storage stability of this prepolymer is at least 6 weeks. Excess concentrations of benzoyl chloride poisons the catalyst, resulting in poor bond strengths. In addition, the prepolymer must be stored in a moisture-free environment.

Curalon L is unsatisfactory as a curing agent or co-curing agent for the isocyanate-terminated prepolymer of perfluoropropylene oxide.

In descending order of reactivity, cobalt, lead, tin, iron, copper, and then manganese can be considered catalysts for the fluorinated polyurethanes. Wide variations in gel time are possibly by varying the catalyst and concentration. High percentages of catalyst result in poor adhesive bonds. Optimum bond strengths were obtained at 0.1% lead or iron, or 0.01% tin. Tin imparts sensitivity to gelation in the adhesive, and produces a very short pot life. Iron or lead catalysts results in adhesives having a good pot life as well as excellent bond strengths, with iron being somewhat superior to lead.

The bond strength of the fluorinated polyurethane adhesive is greatly dependent on curing conditions, with poorer results being obtained when the system is cured at 200°F than at 160°F.

The optimum crosslink density of the fluorinated polyurethane adhesive is at an NCO:OH ratio of 1.6:1, with no apparent differences at higher ratios (to 2:1).

The fluorinated polyurethane from 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene and the polyether of perfluoropropylene oxide is LOX compatible. Excellent bond strengths are obtainable up to 150°F. The system is not suggested for use over 150°F.

## RECOMMENDATIONS FOR FUTURE WORK

Work should be concluded on the optimization of the polyurethane adhesive system prepared from the polyether of perfluoropropylene oxide and 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene.

An amine curing agent should be synthesized to improve the overall adhesive characteristics of the fluorinated polyurethane.

The fluorinated polyurethanes, owing to their unique properties of EOX compatibility and nonflammability, should be evaluated as potting and encapsulating compounds, elastomers, coatings, films, and foams.



## APPENDIX I

### DETERMINATION OF HYDROXYL CONTENT OF POLYETHER FROM PERFLUOROPROPYLENE OXIDE

1. Into each of four flasks, carefully pipette 20 ml of the acetic anhydride-pyridine reagent\*. Use the same pipette for each transfer. Reserve two of the flasks for a blank determination (controls).
2. Into each of the two test flasks, introduce a sample of 6.0 g or less, weighing to the nearest 0.1 mg.
3. Stopper the flasks and heat on a steam bath at  $98^{\circ}\pm 2^{\circ}\text{C}$  for a minimum of 48 hours.
4. Remove the flasks from the bath, cool to room temperature, then add crushed ice until each container is about halfway filled. Wash down the walls with 20-30 ml of distilled water.
5. To each flask, add exactly 50 ml of standard 0.5N sodium hydroxide, agitating vigorously during the addition.
6. Add 1 ml of phenolphthalein indicator and titrate immediately with standard 0.5N sodium hydroxide to the first pink end point, permanent for at least 15 seconds.
7. Calculations

$$\frac{S \times \text{No. of OH Groups} \times 1000}{(B - A) \times N} = \text{Molecular Weight}$$

where S is the sample weight (g)  
B is the amount of sodium hydroxide used  
for blank (ml)  
A is the amount of sodium hydroxide used  
for sample (ml)  
N is the normality of sodium hydroxide used

---

\* The acetic anhydride-pyridine reagent is prepared by adding 57 ml (60 g) of acetic anhydride to 450 ml (440 g) of pyridine and shaking vigorously to obtain complete reaction. One milliliter of distilled water is then added to stabilize the reagent. The reagent is stored in a dark glass-stoppered bottle.

## APPENDIX II

### DETERMINATION OF ISOCYANATE CONTENT OF 1-CHLORO-2,4-DIISOCYANATO-3,5,6-TRIFLUOROBENZENE

1. Weigh out 0.5-1.1 g sample of material to four significant figures. Run duplicates.
2. Add 25 ml of dry toluene to the samples from item 1 and dissolve the samples. Run two blanks.
3. Add 10 ml of approximately 2N dibutyl amine in dry toluene to each flask from item 2.
4. Slowly bring the flasks to a boil with stirring.
5. Cool to room temperature and add 50 ml of methanol.
6. Titrate with approximately 0.1N HCl (of known normality) using bromophenol blue indicator in toluene. End point is the change from blue to yellow-green.
7. Calculations

$$\frac{(B - A) 42 \times N \times 100}{S \times 1000} = \% \text{ NCO}$$

where B is the amount of HCl required to  
titrate blank (ml)

A is the amount of HCl required to  
titrate sample (ml)

N is the normality of HCl

S is the sample weight (g)

### APPENDIX III

#### EXPERIMENTAL BONDING PROCEDURE FOR FLUORINATED POLYURETHANE ADHESIVES

##### Adherend Preparation

1. Stamp adherends from 2024-T3 aluminum in the form of eight specimen breakaway panels, as shown in Figure 7.
2. Remove burrs on edge of panels with file.
3. Remove mill lettering by wiping with methyl ethyl ketone.
4. Degrease, using 10-minute trichloroethylene vapor degrease at 194°-212°F.
5. Etch panels 10 minutes at 151°-160°F. Allow panels to drain 10 to 20 seconds. Etch solution composition: distilled water, 30 pbw; sulfuric acid, 10 pbw; sodium dichromate dihydrate, 4 pbw. Control limits:  $H_2SO_4$  34-42 oz/gal;  $Na_2Cr_2O_7$ , 11-14 oz/gal.
6. Spray-rinse thoroughly with cold tapwater followed by two rinses with running cold distilled water.
7. Oven-dry for 10 minutes at 140°-150°F.
8. Cover panels with clean dry paper until ready for bonding. Bond panels within 6 hours after etching.

##### Bonding Procedure

1. Apply adhesive to both surfaces of mating adherends.
2. Sprinkle 4.1 mil (140-200 mesh) glass beads on bondline, using a salt shaker technique.
3. Unite panels on bonding fixture, using doublers, spacers, and fluorocarbon film separators where necessary (see Figure 8).
4. Vacuum-bag, using envelope bagging technique. Cure overnight (17  $\pm$  2 hours) at room temperature with a vacuum of 10-15 in. Hg. Remove from vacuum bag and postcure at 160°F for 48  $\pm$  1 hour.
5. Number specimens for identification.
6. Cut eight lap shear specimens from each panel.
7. Remove adhesive flash with a trim knife.

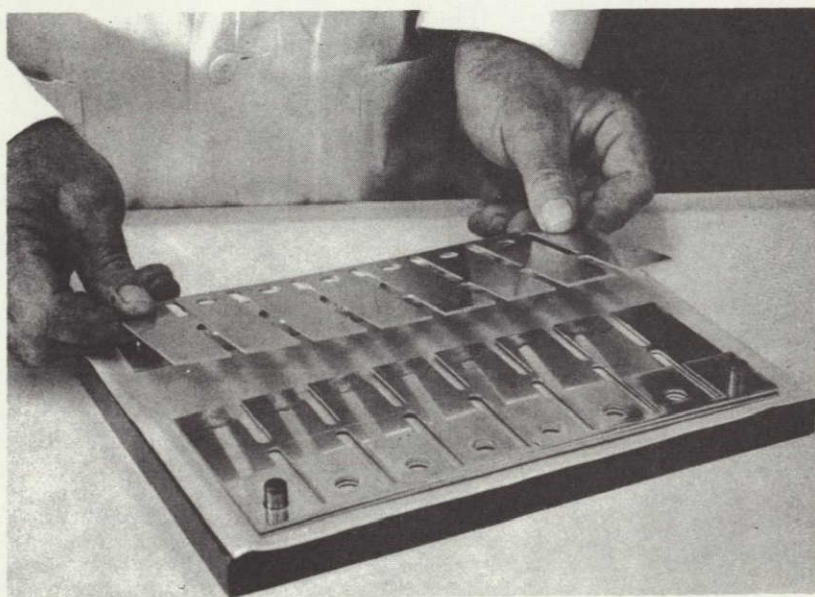
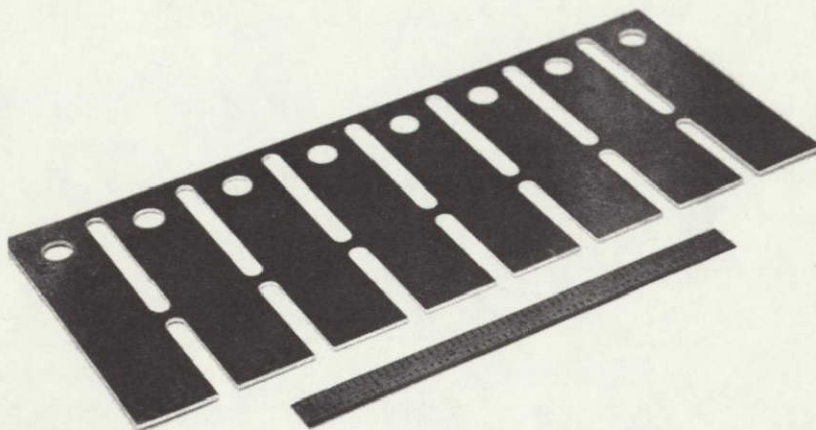


Figure 7. Aluminum Coupons and Assembly Operation for Fluorinated Polyurethane Adhesive

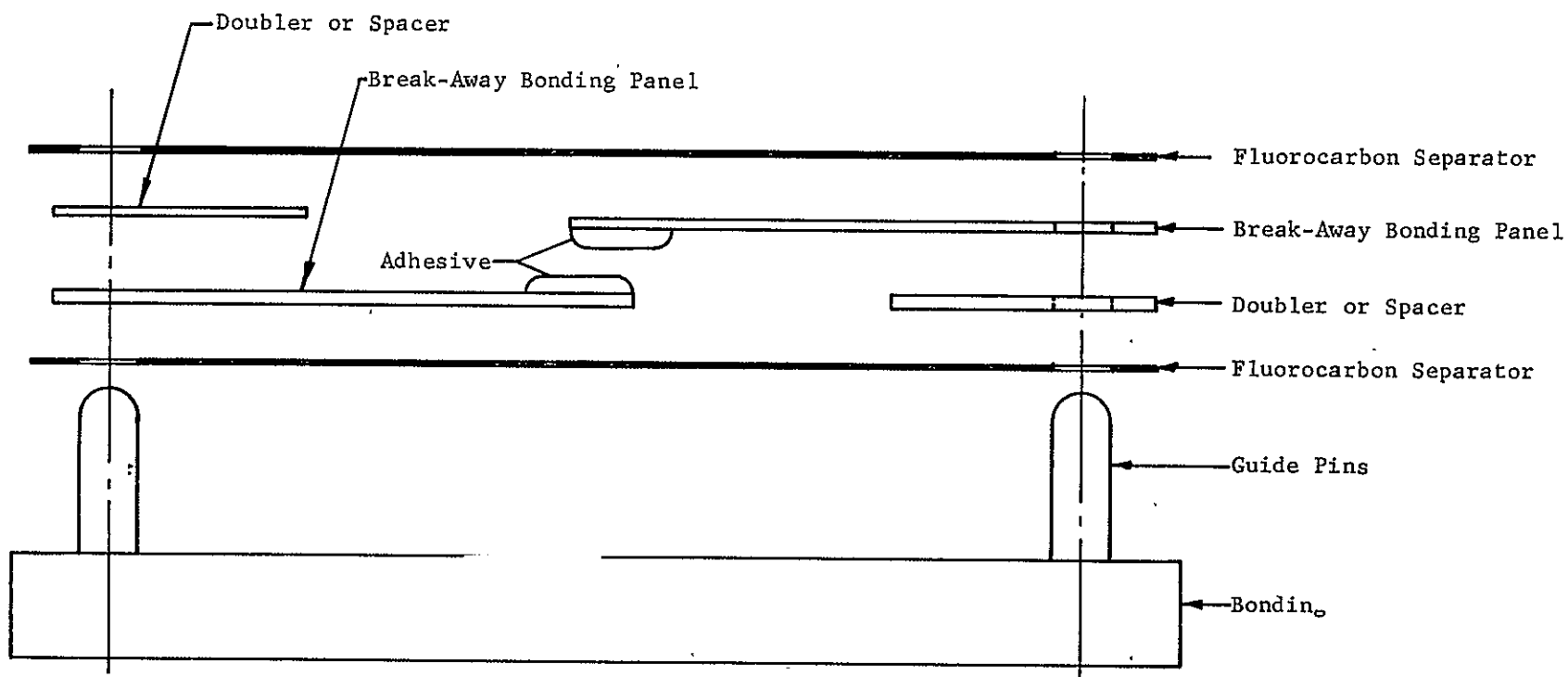


Figure 8. Exploded End View of Bonding Fixture, with One Complete Bonded Panel Assembly

8. Discard all bonds with tilted bondlines or bondlines greater than 7 or less than 3 mils.
9. Test bonds at  $7 \pm 3$  days after layup, per test procedure described in Appendix IV. Bonds tested at  $-320^{\circ}\text{F}$  are submerged in liquid nitrogen.

## APPENDIX IV

### DETERMINATION OF SHEAR STRENGTH OF ADHESIVE-BONDED METAL-TO-METAL SPECIMENS AT ROOM TEMPERATURE AND ELEVATED TEMPERATURES \*

#### 1. Scope

This procedure covers the determination of the tensile shear strength of adhesive-bonded metal-to-metal specimens when tested at room and at elevated temperatures.

#### 2. Related Documents

MIL-A-5090D

Federal Test Method Standard No. 175, Method 1033

ASTM D1002

#### 3. Test Specimens

3.1 The test specimens shall conform to the shape and dimensions shown in Figure 9.

#### 4. Specimen Preparation

4.1 Test specimens shall be made to the final configuration (Figure 9) by cutting a bonded panel (using a band saw)(Figure 10) through the slots provided.

4.2 The cutting of the specimen shall avoid overheating and/or mechanical damage to the joints.

4.3 The specimens shall be prepared so that adherends are flat and parallel, providing a glueline of uniform thickness. Specimens with a variation in glueline thickness in excess of 20% of the average thickness shall be rejected, identified as unsuitable for testing, and returned to the requester. Specimens shall be properly aligned so that an imaginary line between the centers of the end holes bisects the overlap area. Specimens not properly aligned shall be rejected, so identified, and returned to the requester.

4.4 If the strength of the adhesive is such that it will cause deformation or failure of the metal at the pin hole, doublers may be added. For steel specimens, steel washers (0.062 in. thick with a 0.375 in. hole) spotwelded to the specimen are satisfactory. Unplated washers shall be used.

For aluminum panels, the doublers must be bonded to the specimens, preferably when the lap joint is prepared. The doublers shall be of the same material from which the specimen is made.

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\*This is Whittaker Engineering Test Method No. 401.

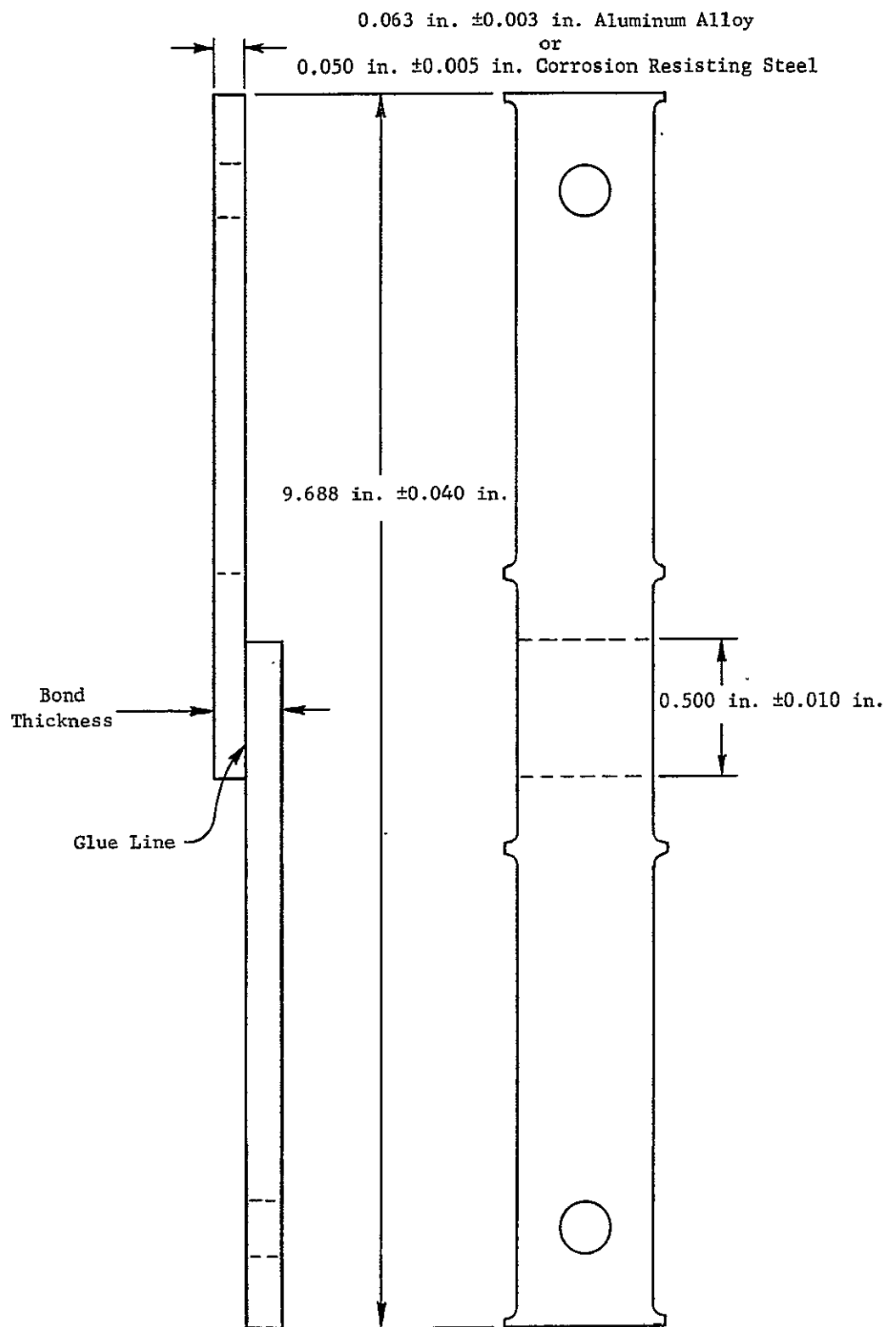


Figure 9. Test Specimen



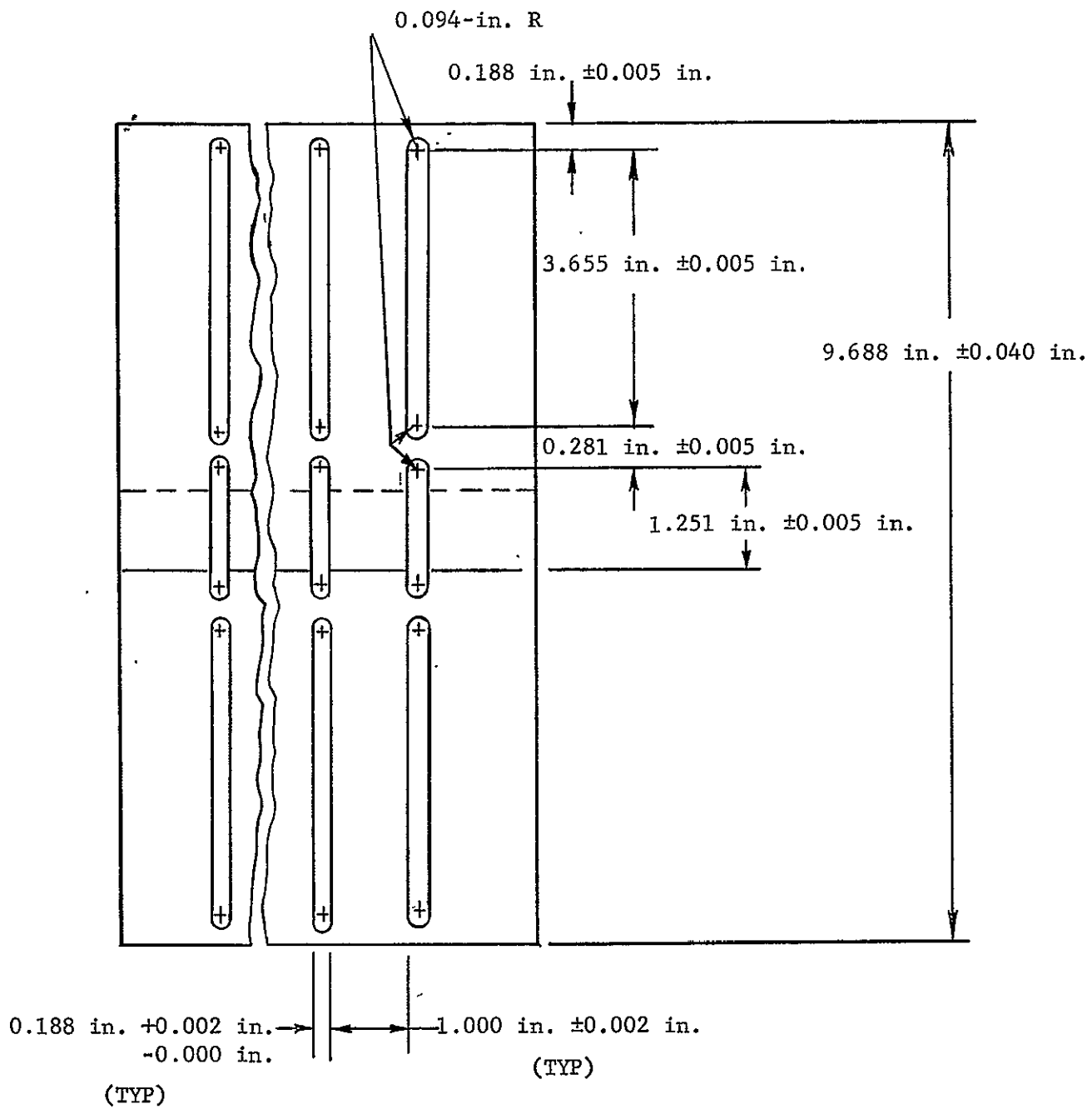


Figure 10. Preferred Assembled Panel

- 4.5 If the adhesive strength is such that failures consistently occur in the metal, a reduced bonded area may be used. When a definite strength value for the adhesive must be determined, a lap length of 0.375 in.  $\pm 0.010$  in. shall be used in place of the standard 0.500 in.  $\pm 0.010$  lap length shown in Figure 9.

## 5. Specimen Conditioning

- 5.1 Since conditioning is not required for metal-to-metal bonds, specimens shall be tested as soon after preparation as possible.

## 6. Apparatus

- 6.1 Testing Machine — A testing machine having a controllable crosshead speed and properly calibrated load indicator shall be used.
- 6.2 Fixtures — A set of clevis type grips with pins 0.375 in. in diameter shall be used (Figure 11).
- 6.3 Thermocouple and Potentiometer — For tests at elevated temperatures, the temperature of the test specimen shall be determined utilizing a prototype, or dummy specimen. This specimen shall be prepared by placing the junction of an iron-constantan thermocouple in the center of the overlap area between the adherends prior to bonding (see Figure 12). The adherend material shall be the same as that of the specimens being tested.

The thermocouple shall be connected to a properly calibrated potentiometer.

- 6.4 Heat Source — One of the following two heat sources shall be selected for elevated temperature testing.

6.4.1 An oven adequate for use with the test machine and equipped with controls for maintaining the test temperature within 2% shall be used.

6.4.2 Quartz lamps may be used, arranged in two banks on either side of the test specimen, as shown in Figure 13. The voltage to the lamps shall be controllable with a powerstat.

## 7. Procedure

- 7.1 Room temperature testing — Using pertinent information from the Test Request and test specifications, prepare a test data sheet.

7.1.1 Measure the thickness of both adherends adjacent to the lap joint and the bond thickness (Figure 9) to the nearest 0.0001 in. and record the values.

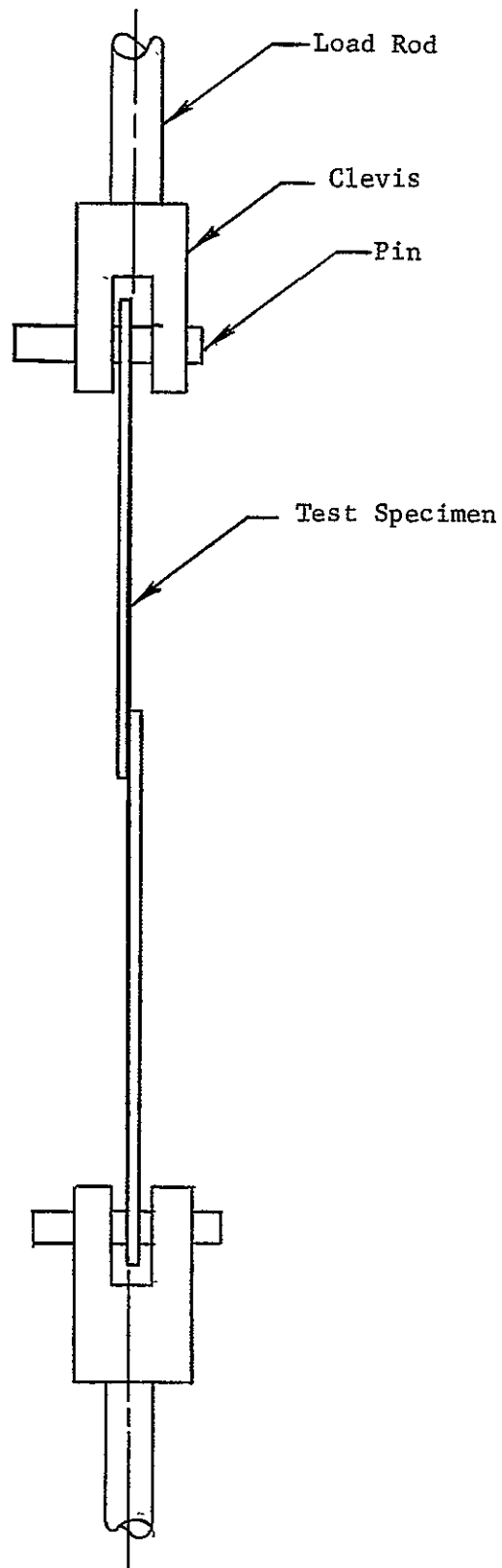


Figure 11. Test Fixture

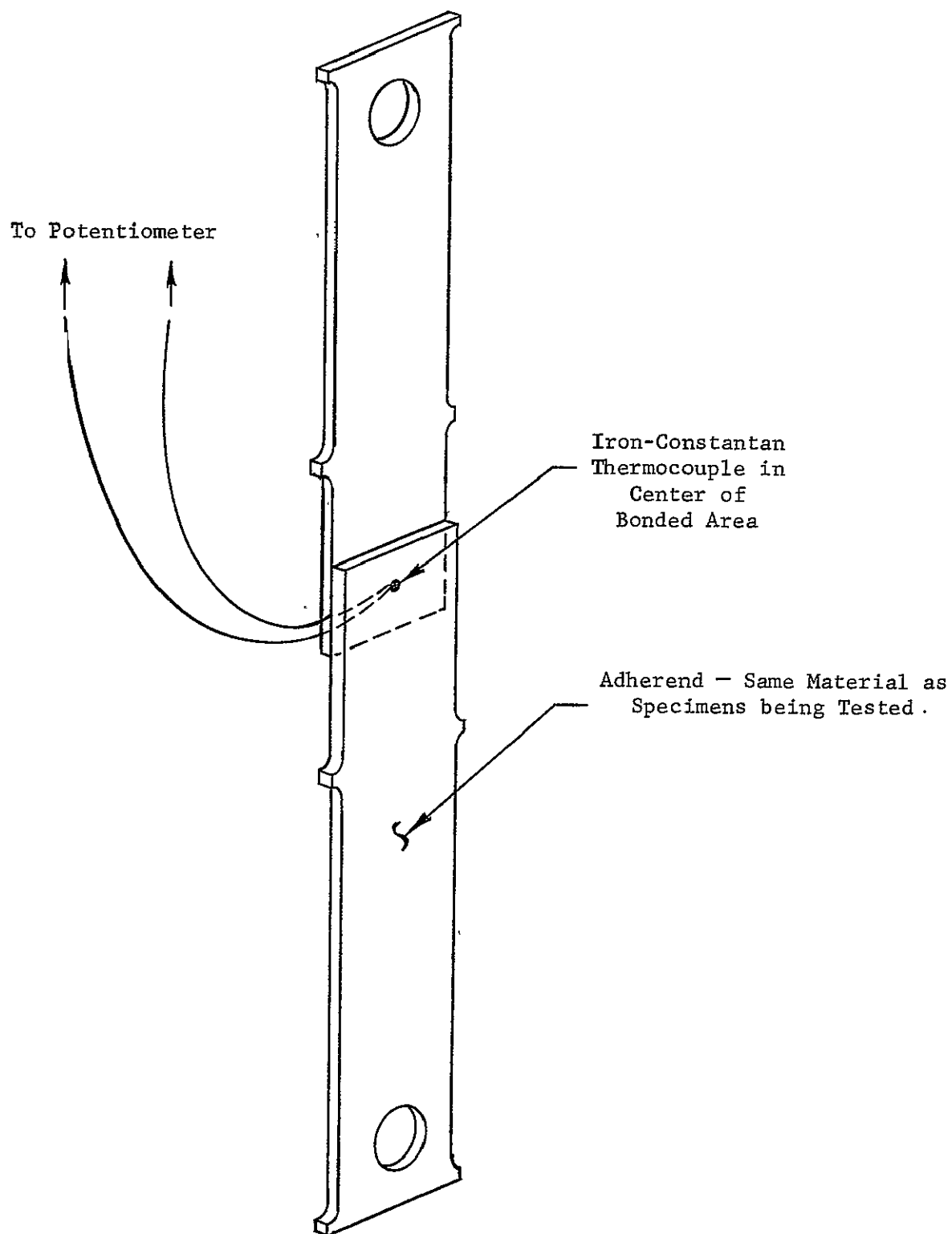


Figure 12. Prototype Specimen

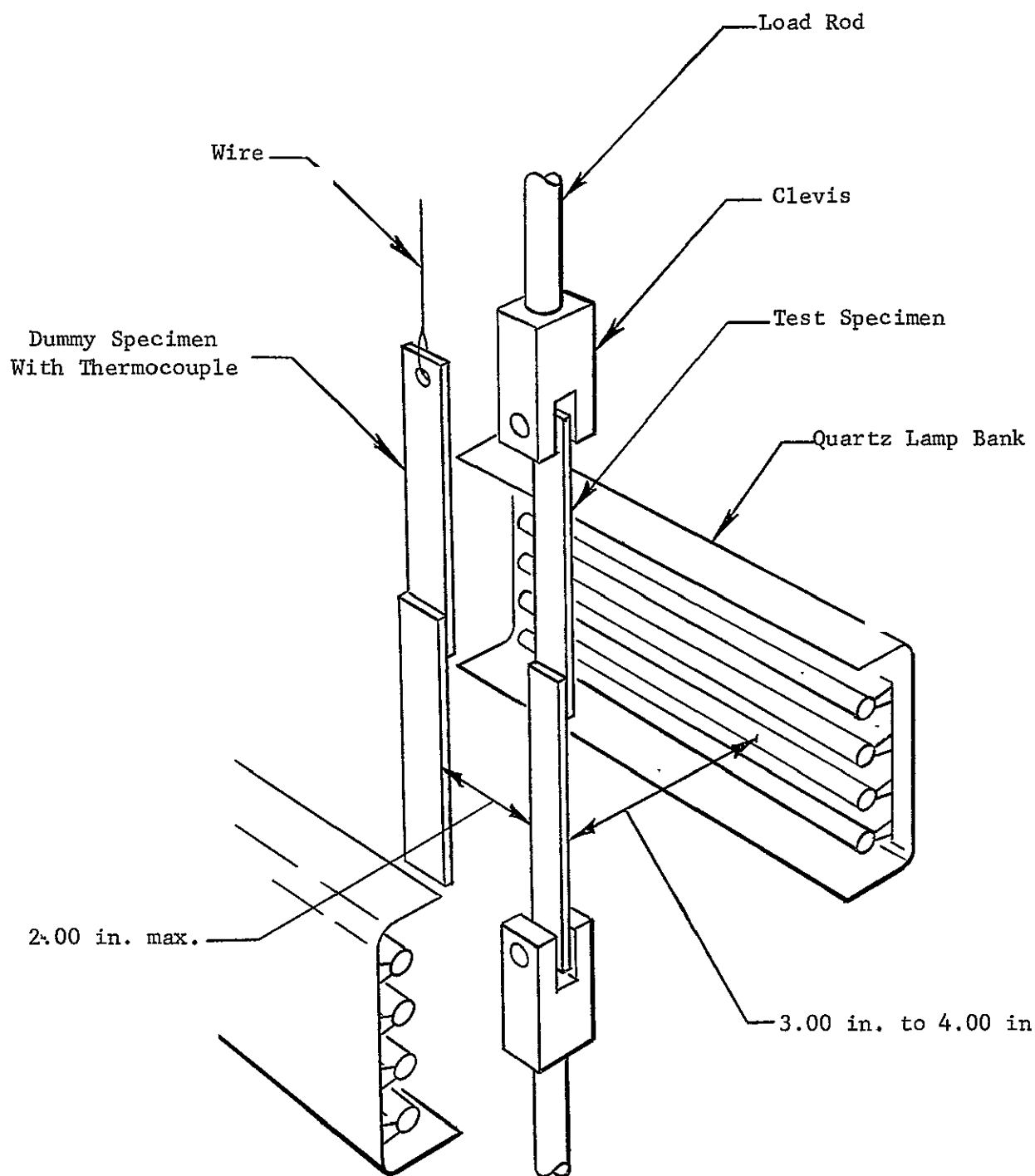


Figure 13. Test Apparatus Assembly

- 7.1.2 Determine the glueline thickness by subtracting the sum of the adherend thicknesses from the bond thickness. Record the value on the data sheet.

Care shall be taken to avoid errors in thickness measurements due to adhesive flash, or other excess material adhering to the metal surface.

- 7.1.3 Assemble the test specimen in the grips of the testing machine so that the long axis of the test specimen coincides with the direction of applied pull through the centerline of the grip assembly (Figure 11).
- 7.1.4 Select before testing, the load range which is likely to provide the most accurate results.
- 7.1.5 Set the test machine to a crosshead speed of 0.020 in.  $\pm$  0.002 in minute.
- 7.1.6 Record the maximum load carried by the specimen during the test. Notation of improper failure or other pertinent comments shall be recorded.

7.2 Elevated Temperature Testing - Prepare a test data sheet, using pertinent information from the Test Request and test specification.

- 7.2.1 Measure the thickness of both adherends adjacent to the lap joint and the bond thickness (Figure 9) to the nearest 0.0001 in. and record the values.
- 7.2.2 Determine the glueline thickness by subtracting the sum of the adherend thicknesses from the bond thickness. Record the value on the data sheet.

Care shall be taken to avoid errors in thickness measurements due to adhesive flash, or other excess material adhering to the metal surface.

- 7.2.3 Assemble the test specimen in the grips of the testing machine, so that the long axis of the test specimen coincides with the direction of applied pull through the centerline of the grip assembly (Figure 11).

The dummy specimen with thermocouple installed shall be suspended from a wire so that the bonded area is at the same height as the test specimen, and located not more than 2 in. from the test specimen (see Figure 13).

- 7.2.4 Select before testing, the load range which is likely to provide the most accurate results.

- 7.2.5 Set the test machine to a crosshead speed of 0.020 in.  $\pm$ 0.002 in./minute.
- 7.2.6 Heat the prototype specimen to the test temperature,  $\pm$ 2% as indicated by the thermocouple and potentiometer. The specimen shall be held at the test temperature for 1 minute prior to testing.
- 7.2.7 Record the maximum load carried by the specimen during the test. Notation of improper failure or other pertinent comments shall be recorded.

## 8. Calculations

- 8.1 Tensile Shear Strength — The tensile shear strength shall be calculated by dividing the maximum load in pounds by the shear area in square inches. The results shall be expressed in pounds per square inch (psi) and recorded to three significant figures. The following equation shall be used:

$$F_s = \frac{P}{A}$$

$F_s$  = tensile shear strength (psi)

$P$  = maximum load carried by the specimen (lb)

$A$  = shear area (in.)

## 9. Report

- 9.1 The report shall include the following:
  - 9.1.1 Complete identification of the material tested, including type, source, etc.
  - 9.1.2 Complete identification of the specimen including bond length, width and area, glue line thickness, and adherend material and thickness.
  - 9.1.3 Method of testing the specimen
  - 9.1.4 Temperature of test
  - 9.1.5 Identification of test machine and potentiometer used
  - 9.1.6 Number of specimens tested
  - 9.1.7 Ultimate tensile shear strength, average value

9.1.8 Nature of failure, including the average estimated percentages of failure in the cohesion of the adhesive, contact failure, and adhesion to adherend

9.1.9 Date of test

NOTES:

- (1) The test data shall be reviewed and approved by the test engineer in charge of the program before releasing it; however, "preliminary" information may be furnished to the requester with the approval of the test engineer.
- (2) The test data shall not be considered final until issued in an approved test report form.
- (3) The original test data sheet with the corresponding charts attached shall be kept on file in Engineering Test..



## APPENDIX V

### PROCEDURE FOR DETERMINING THE FREE ISOCYANATE CONTENT OF THE ISOCYANATE-TERMINATED PREPOLYMER OF PERFLUOROPROPYLENE OXIDE

1. Weigh out 0.5-1.1 g sample of the prepolymer to four significant figures. Run duplicates.
2. Add 25 ml of dry tetrahydrofuran to the samples from item 1 and dissolve the samples. Run two blanks.
3. Add 2.0 ml of approximately 2N dibutyl amine in dry toluene to the flasks from item 2.
4. Allow the mixture from item 3 to stand for 10 to 30 minutes maximum.
5. Add 50 ml of methanol.
6. Titrate with approximately 0.1N HCl (of known normality) using bromophenol blue indicator in toluene. End point is the change from blue to yellow-green.
7. Calculations.

$$\frac{(B - A) 42 \times N \times 100}{S \times 1000} = \% \text{ NCO}$$

where B is the amount of HCl required to  
titrate blank (ml)  
A is the amount of HCl required to  
titrate sample (ml)  
N is the normality of HCl  
S is the sample weight (g)